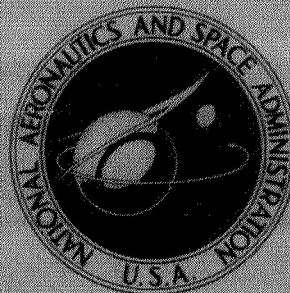


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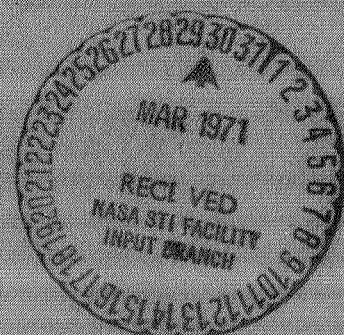
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**CONTROL OF NITROGEN DIOXIDE
IN STACK EMISSION
BY REACTION WITH AMMONIA**

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16. Abstract <p>Research rocket operations released nitrogen-dioxide (NO₂)-containing stack gases to the atmosphere. To eliminate the potential hazard of this release, a gas-phase reactor system was developed which used anhydrous ammonia to convert the NO₂ to ammonium nitrate. When an excess of ammonia was used, a reaction time of about 7.5 seconds resulted in the removal of an estimated 99 percent of the NO₂ initially present. An exhaust treatment system is proposed which would recover the excess ammonia and remove the ammonium nitrate formed, so that the exhaust emission would probably not be visible.</p>					
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CONTROL OF NITROGEN DIOXIDE IN STACK EMISSION

BY REACTION WITH AMMONIA

by Allen J. Metzler

Lewis Research Center

SUMMARY

Research operations vented brown clouds of gases containing nitrogen dioxide (NO_2) to the atmosphere. The NO_2 concentration was estimated to be near 15 000 parts per million. This could be a potential community health problem and was not acceptable, so a method of removing the objectionable NO_2 was required. The gases emitted to the atmosphere were to have no brown coloration, which meant that more than 99 percent of the original NO_2 had to be removed so that the residual concentration in the emission would be below the visible limit of about 100 ppm.

The kinetics of the gas-phase reaction of NO_2 and ammonia to form ammonium nitrate, as reported in the literature, was applied to the exhaust flow conditions. This indicated that the required removal effectiveness might be accomplished within a time period of the same order as the exhaust residence time within the ducting. A gas-phase reactor was designed and installed in the existing exhaust system, and the test results are reported. Reaction times of about 1 second and 7.5 seconds were used, and ammonia flow was greater than the stoichiometric requirement. Visual observation of the exhaust stack exit indicated that the exhaust was still highly colored when the reaction time was limited to only 1 second. With the longer reaction time, at least 99 percent of the NO_2 initially present was apparently removed and the exhaust was white. The system reported was not refined and further improvements are possible.

A gas scrubber addition is suggested to remove the solid products of the reaction, to improve the reaction effectiveness, and to possibly render the system economically attractive for some industrial pollution abatement requirements.

INTRODUCTION

The release of nitrogen dioxide (NO_2) from research facilities to the atmosphere has been a troublesome problem at the Lewis Research Center. The discharge of large quantities of NO_2 to the atmosphere is unacceptable because of possible community health problems, and because the increased awareness to air pollution has increased the sensitivity of the community to the problem. Nitrogen dioxide is an intensely colored brown gas which is readily visible in even low concentrations. However, the color, or apparent optical density, is not an acceptable criterion for estimating the concentration of NO_2 in a gas mixture. Although an NO_2 concentration of 50 ppm is generally considered to be the lower limit for visibility, for long optical paths, such as the observation of the Los Angeles sky, a visible brown coloration can be observed with only 0.25 ppm of NO_2 present in the gas mixture (ref. 1). A colored emission, therefore, is not necessarily a potential health hazard since the threshold limit value (TLV) for long-term human exposure is generally accepted to be near 5 ppm. For individuals with respiratory problems, the NO_2 tolerance level might be appreciably lower. Thus, to eliminate all possibility of hazard to the surrounding communities, a system was needed to remove the NO_2 from high-volume-flow research facility exhaust gases before they were vented to the atmosphere.

It was recognized that high-stack venting has the potential of promoting rapid atmospheric dilution of even high-concentration NO_2 mixtures (ref. 2), but a temperature inversion could negate such an effect. High-stack venting, therefore, was considered only as an adjunct to a basic system required to remove NO_2 from the stack gases. Gases emitted to the atmosphere were to have no brown coloration.

Chemically, NO_2 is an acid-oxidizer and can be removed by either acid-base or combustion reaction processes. The removal of NO_2 from rocket exhaust gases by sodium hydroxide absorption was considered, as well as reaction in a fuel-rich burner as discussed in reference 3. For high-volume-flow-rate systems, such schemes are impractical because of the large and expensive reactor which would be required to ensure the almost complete removal of the NO_2 gas.

A gas-phase reaction system which utilized anhydrous ammonia as the reactant to remove NO_2 was developed. Ammonia was selected because of its effectiveness and because of its practicality for use in a high-volume-flow system. Preliminary analyses indicated that the efficiency of NO_2 removal would depend on both reaction time and ammonia concentration and suggested a design to optimize the NO_2 - NH_3 reaction. Although the system design and performance was not fully optimized, the reaction effectiveness in removing NO_2 was demonstrated in limited testing, and the preliminary results are reported herein. In the tests reported, the NO_2 level was so reduced that the resulting emission was colorless. Although the system described was developed

specifically for a particular high-volume-flow-rate application, design improvements which are proposed should not only improve the reaction effectiveness, but should also make the system more economically attractive for industrial application.

This report briefly documents the performance and development of a practical system for the removal of NO_2 gas from research facility exhaust emissions so that this information might serve as timely guidance to others in the research-and-development community faced with similar problems. This work was conducted at the Lewis Research Center, Cleveland, Ohio.

NITROGEN DIOXIDE SOURCE AND REMOVAL PROBLEM

Nitrogen Dioxide Source

A test facility for an advanced combustor research program utilized an oxidant-rich hydrazine - nitrogen tetroxide rocket as a gas-generating device (ref. 4). The rocket operation introduced free NO_2 into the exhaust gas, which was discharged at atmospheric pressure through either of two stacks. One was an air ejector with an exit 23.8 meters (78 ft) above grade level, but the exhaust velocity effectively doubled this height. In preliminary tests, large, reddish-brown clouds formed above this stack and dispersed slowly. The other stack was a low-velocity chimney 5.2 meters (17 ft) in diameter and 15.2 meters (50 ft) high.

The emission at the stack exit was to be colorless. It was determined that the free nitrogen dioxide in the exhaust gases should be removed during passage through the exhaust system between the last compressor stage and the stack exit. This part of the exhaust system is diagrammatically shown in figure 1, together with the flow conditions estimated for this portion of the system.

Approximately 45.6 meters (150 ft) of 1.2-meter- (4-ft-) diameter piping connected the exit of the final compressor stage with the base of the exhaust stacks. The gas flow rate of 68 kilograms per second (150 lb/sec) was at near-atmospheric pressure and consisted of water vapor, NO_2 , nitrogen, and oxygen. About one-third of the mass-flow rate at the compressor exit was dilution air. The average flow rate of NO_2 did not exceed 2.6 kilograms per second (5.7 lb/sec) except during rocket starts. Residence time within the 45.6 meters (150 ft) of ducting was calculated to be 0.8 second. The residence time in the low-velocity stack was 6.7 seconds, as indicated.

The exhaust flow could alternatively be diverted to an air ejector driven by 29.4 kilograms per second (65 lb/sec) of compressed air. The stack exit velocity was about 30.5 meters (100 ft) per second and resulted in an effective stack height of 62.5 meters (205 ft), as calculated according to reference 2; but it limited the residence time to only

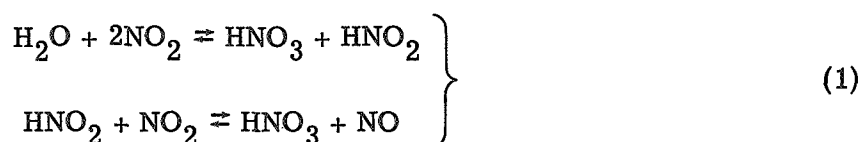
0.2 second within the ejector stack. The total transit time within the piping was, therefore, only 1 second for ejector stack exhaust as compared to 7.5 seconds for exhaust venting through the low-velocity chimney stack.

The concentration of free NO_2 at the exit of the ejector stack was estimated to be near 15 000 ppm for the flow conditions assumed. Such concentrations would be expected to, and did in fact, appear as very dark brown clouds. The apparent color density or opacity of NO_2 is a function of the product of concentration and the optical absorption path length, and it was estimated (by R. Hibbard of Lewis) that NO_2 -containing gas mixtures would appear light brown if this product was approximately 3.05×10^3 ppm-meters. From a 1.8-meter- (6-ft-) diameter stack, 1600 ppm would also appear brown, so that at least a 160-fold reduction in the initial NO_2 concentration was required to approach the visible concentration limit of about 100 ppm. On-line analysis was not available to monitor stack effluent for these tests, although an instrument suitable for NO_2 concentrations ranging from 0.1 to 15 000 ppm is described in reference 5.

Nitrogen Dioxide Removal Reactions

Nitrogen dioxide is a strong oxidizer and will readily burn in a fuel-rich flame to form free nitrogen and water as products (refs. 3 and 6). Burner design and operation for high-mass-flow-rate and relatively dilute NO_2 systems are complex and costly, and are especially so for intermittent, non-steady-flow conditions. Therefore, NO_2 removal by flame reaction was deemed impractical.

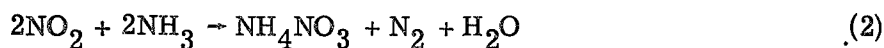
Nitrogen dioxide is moderately water soluble to form nitric acid, but it is not an anhydride of the acid. The absorption can be expressed by the equilibria



The absorption is not rapid and does not result in complete removal of NO_2 . Complete removal would be favored by the neutralization of the acid reaction products. Scrubbing with sodium hydroxide solution, however, did not satisfactorily remove NO_2 from a small-scale rocket test facility (private communication with W. Kerslake of Lewis), presumably because of the relatively slow conversion of the NO_2 to the acid. Therefore, this scheme for removal was also considered impractical for this application.

A third mechanism for the removal of NO_2 is the gas-phase reaction with anhydrous ammonia, as discussed in references 7 and 8. At temperatures below 200°C , the main

reaction product is ammonium nitrate. At low pressures, as least 99 percent of the product is formed according to



Only traces of ammonium nitrite (NH_4NO_2) are formed, and this may originate from the side reaction between the NO_2 and the water formed from the main reaction (2). The references indicate the initial reaction to be third order. During the course of reaction, however, the rate changes and the reaction accelerates. The reaction has a strong negative temperature coefficient with an apparent activation energy of -12.5 ± 1.0 kilocalories per mole ($(-5.23 \pm 0.42) \times 10^4$ J/mole). This results in the following third-order specific rate constants for the reaction:

Temperature, °C	Reaction rate constant, $\text{cm}^6/(\text{mol}^2)(\text{sec})$
205	2.2×10^9
151	1.1×10^{10}
27	4.5×10^{12}

The reaction time for the ammonia - nitrogen dioxide reaction was calculated for several flow conditions. This time was then compared with the calculated exhaust residence time within the piping system in order to determine the feasibility of the reaction system and to optimize the system design criteria. It was assumed that the reaction did not accelerate but remained constant with a specific rate constant of $4.5 \times 10^{12} \text{ cm}^6/(\text{mol}^2)(\text{sec})$. The reaction was also assumed to proceed from an initial concentration of NO_2 of near 20 000 ppm to a final concentration of 50 or 100 ppm. Ammonia concentrations were stoichiometric, or constant and in excess.

Using only a stoichiometric quantity of NH_3 resulted in exceedingly long reaction time to attain a final NO_2 concentration of 100 ppm. The assumption of a reaction with an ammonia excess is more realistic, since in a practical reactor the ammonia flow would probably be preprogrammed and be independent of the existing NO_2 concentration. For the case where the ammonia concentration is maintained in excess so that its concentration can be considered constant, the time required for reacting from the initial concentration $[\text{NO}_2]_0$ to the final $[\text{NO}_2]_F$ may be estimated from

$$t = \frac{1}{k [\text{NH}_3]} \left\{ \frac{1}{[\text{NO}_2]_F} - \frac{1}{[\text{NO}_2]_0} \right\} \quad (3)$$

for the assumption of a constant specific reaction rate. It is apparent, then, that the reaction time is inversely dependent on the reaction rate, the ammonia concentration, and the final concentration of NO_2 . Also, the final concentration may be minimized by long reaction time with an excess of NH_3 . For an ammonia concentration of 4.85×10^{-6} mole per cubic centimeter reacting to a residual NO_2 concentration of 100 ppm, a reaction time of 11 seconds was calculated assuming a constant reaction rate. This reaction time is of the same order as the residence time of the exhaust flow between the compressor exit and low-velocity-stack exit as shown in figure 1, so the reaction system appeared practical and feasible.

NH_3 - NO_2 REACTOR DESIGN AND RESULTS

The ammonia- NO_2 reaction was first investigated in a small-scale experiment. NO_2 and NH_3 were passed into a glass tube to mix and react according to equation (2) to form NH_4NO_3 . The experiment was repeated with moisture added as an additional reactant to satisfy equations (1). These tests indicated essentially instantaneous reaction, as evidenced by the immediate formation of a white smoke at the point of reactant mixing in both the wet and dry reactions. Both reaction systems appeared to be equally effective, but the smoke of the dry reaction had a slight tinge of gray coloration.

An ammonia reactor system for the removal of free NO_2 from the facility exhaust was designed and installed into the exhaust ducting. The ammonia injectors were located immediately downstream of the last compressor to provide the maximum residence time within the ducting (fig. 1). The exhaust from the reactor section could be diverted to either stack, with a resultant change in reaction, or residence, time. For design purposes the maximum flow rate of free NO_2 at the reactor was assumed to be 2.6 kilograms per second (5.7 lb/sec) in a total mass flow of 68 kilograms per second (150 lb/sec). Liquid NH_3 at 2.3 kilograms per second (5 lb/sec) assured an excess of reactant (somewhat greater than twice stoichiometric), and the addition of 1.6 kilograms per second (3.5 lb/sec) of steam provided heat to ensure ammonia vaporization.

Ammonia and steam were injected into the exhaust gas at seven points in a plane across the 1.2-meter - (48-in.-) diameter duct, as shown in figure 2(a). The three injector manifolds were 5-centimeter- (2-in.-) diameter pipes equally spaced on 35.6-centimeter (14-in.) centers and connected to a common ammonia supply. At each of the seven injection points, the manifold was drilled and fitted with a steam line, as shown in detail in figure 2(b). Liquid ammonia was injected through the 0.076-centimeter (0.030-in.) annulus around the steam line and was vaporized by the 12 steam jets located around the periphery of the pipe as shown. Steam flow rate was constant, but ammonia flow rate was manually varied.

The steam flow rate was excessive and could probably have been eliminated if additional reactor length had been available to accomplish the ammonia vaporization and mixing provided by the steam jets.

Reactor gases were first vented to the atmosphere through the ejector stack. The gases were incompletely reacted, and the stack emission was still highly colored. These results suggested that the available reaction time was inadequate for the $\text{NH}_3\text{-NO}_2$ reaction to proceed to completion before dilution by the ejector air and the atmosphere effectively stopped reaction. The presence of an excess of ammonia in the gas mixture was confirmed by gas analysis.

Venting the reactor through the low-velocity stack increased the available reaction time within the ducting by a factor of about 7, with no dilution of the reactants with additional airflow. This resulted in apparently complete treatment of the gases, as evidenced by a dense white cloud which was emitted at the stack exit. No brown coloration was evident. The elimination of the dilution effect of the ejector air and the increase of the reaction time was sufficient to permit the $\text{NH}_3\text{-NO}_2$ reaction to approach completion and to convert the NO_2 to NH_4NO_3 . The effectiveness of the ammonia in removing NO_2 from the exhaust stream is markedly shown in figure 3. The dark brown emission from the ejector stack before the ammonia reactor was used is shown in figure 3(a). In contrast, the emission from the low-velocity stack, following treatment, was dense and white with the appearance of a billowy cloud of steam (fig. 3(b)).

The effectiveness of long reaction time for the $\text{NH}_3\text{-NO}_2$ reaction was also demonstrated in a nonpumped atmospheric rocket test facility (fig. 4). An oxidant-rich 8.9×10^4 -newton (20 000-lbf) thrust rocket was fired into the large-volume atmospheric exhaust collector shown in the figure, and ammonia was sprayed through a spray station upstream of the muffler. The resulting exhaust was white with no evidence of free NO_2 .

TREATMENT SYSTEM IMPROVEMENTS

The immediate requirement for this particular development was a system to remove NO_2 from gases exhausted to atmosphere during research rocket tests. These test firings were of 20 seconds duration and averaged only one or two per day. Therefore, for such test periods the very dense white cloud containing dispersed nitrate would not be expected to be troublesome and the excess NH_3 usage would not be an economic problem. By recovering and using the excess ammonia, however, the efficiency and economics of this system might make it attractive for the treatment of some industrial waste gases.

A long-term emission of even a white cloud of nitrates and free NH_3 would probably be as unacceptable as brown NO_2 emissions with respect to present air quality standards. However, the nitrates and ammonia could both be eliminated by addition of a water

scrubber. With no compromise to the basic NH_3 - NO_2 reaction system, scrubbers of various designs might be used. The scrubber design shown in figure 5 would be compatible with the low-velocity-stack system used in these tests. The scrubber would remove the finely divided solid salts as well as the excess NH_3 . Stack gases would be non-polluting and probably would not be visible. This scrubber design uses a high-contact-area water curtain or absorption tower to remove both the solids and free NH_3 . The water would be collected in a sump and be recirculated. The ammonia thus recovered would be effective in scrubbing any remaining unreacted NO_2 or acid from the gas stream. Ammonia would be conserved; but more importantly, the scrubber would act as a large ammonia reservoir, or reaction surge tank, with the capability of absorbing large quantities of NO_2 which might otherwise be untreated as a result of either failure of the primary treatment system or a sudden surge from the NO_2 source. The scrubber would be the safety valve to the emission control system and utilize, as an integral part of the treatment system, the ammonia excess which would otherwise go unrecovered.

CONCLUDING REMARKS

The removal of NO_2 from stack emissions is a problem in the research community as well as in industry. The impetus of improved air quality has put increased emphasis on requirements for improved treatment of all types and quantities of atmospheric emissions. The high degree of visibility of NO_2 and its contribution to the problem of smog in large urban areas makes the emission of NO_2 -containing stack gases particularly vulnerable to criticism. The high degree of visibility of NO_2 also makes the removal problem severe since "clean" emission in the case of NO_2 means complete removal of NO_2 , for all practical purposes. Partial removal of the offending NO_2 from gases is only little better than no removal.

The system for removal of nitrogen dioxide which is reported herein was, as originally developed, a first approach to a problem and was not economically refined. The system was effective, and stack gases were uncolored. The residual NO_2 level was believed to be less than 1 percent of the level prior to treatment. Improvements described herein would not only make treatment more effective for the research type of requirement, but might also make the system effective and economically attractive for some industrial pollution abatement requirements.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 7, 1971,
722-03.

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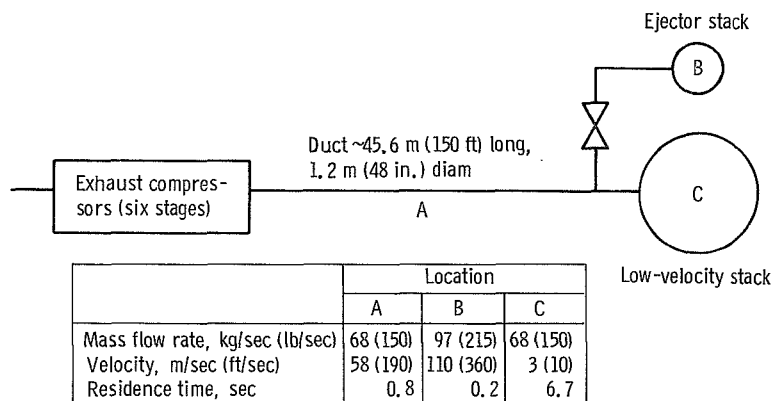
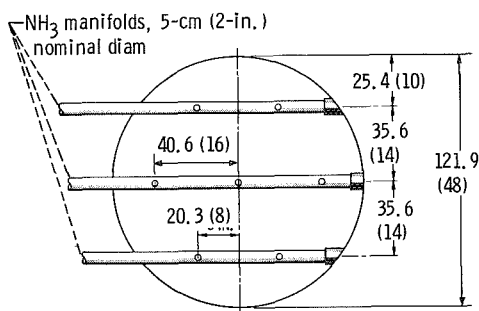
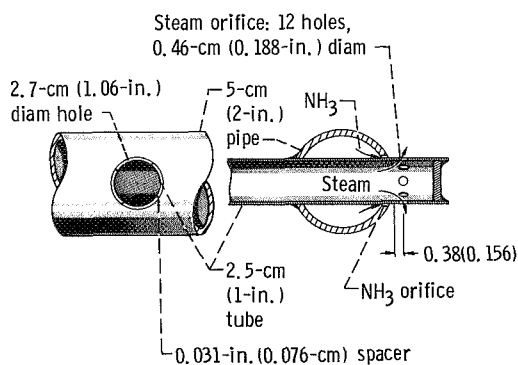


Figure 1. - Exhaust system schematic.

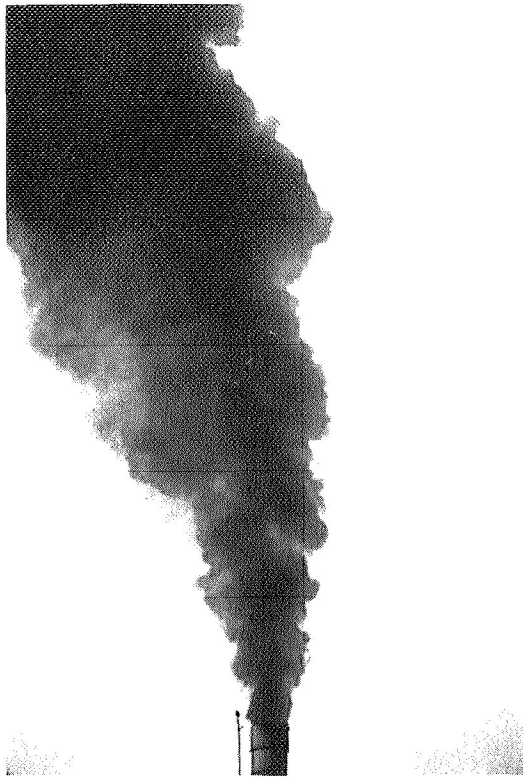


(a) Distribution of injection locations.

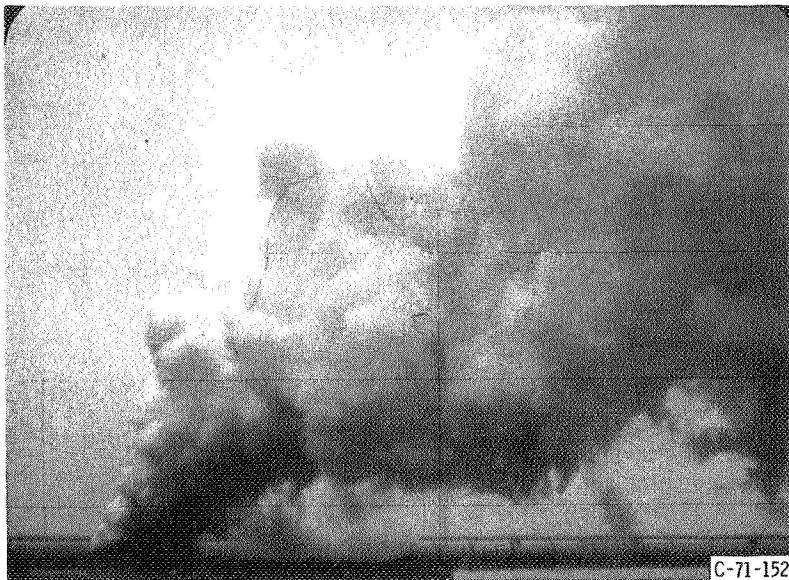


(b) Detail of injector construction.

Figure 2. - Ammonia-steam injector. (Dimensions are in cm (in.).)



(a) Ejector stack - before ammonia treatment.



(b) Low-velocity stack - after ammonia treatment.

Figure 3. - Exhaust emission at stack exits.

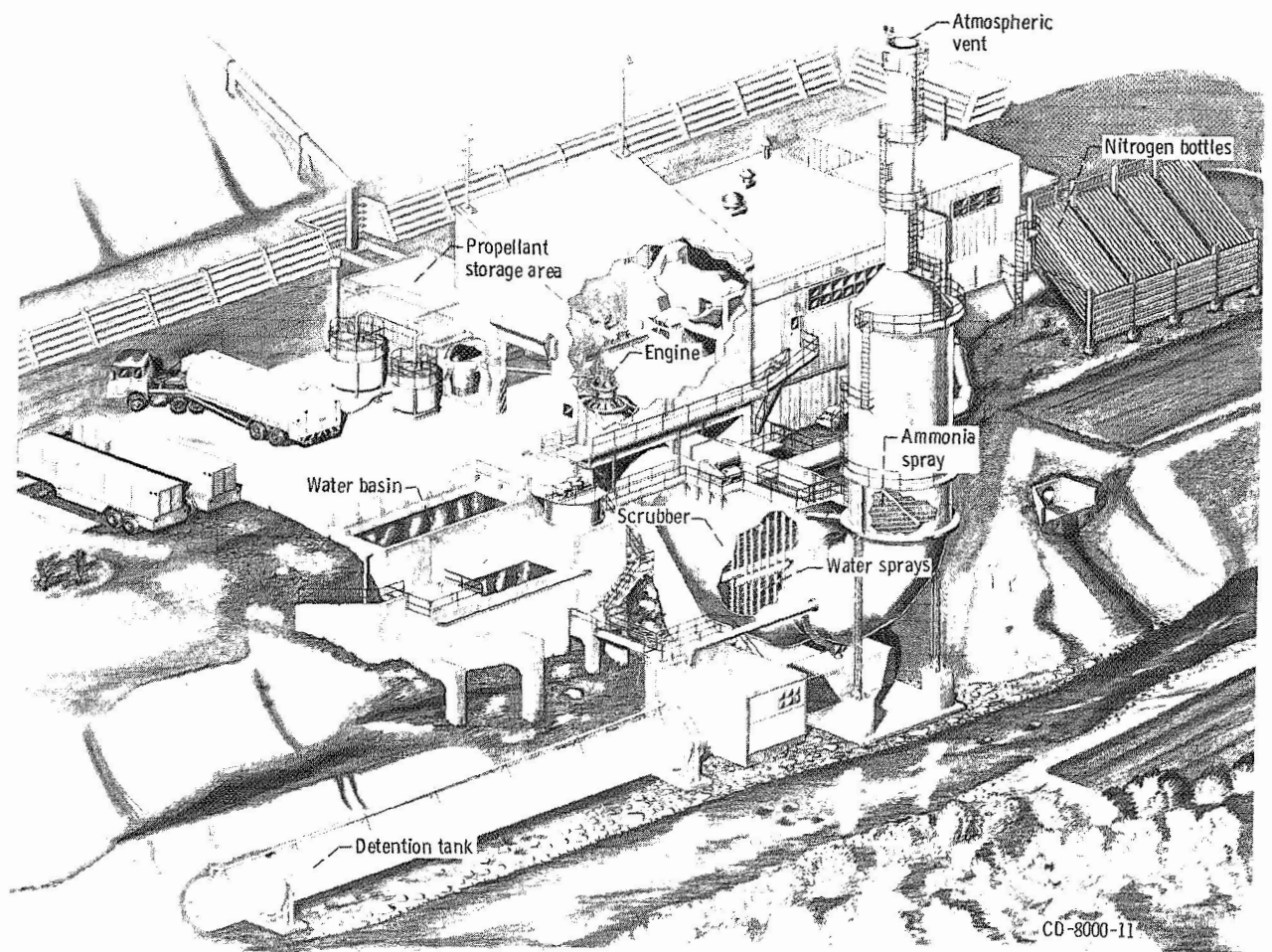


Figure 4. - Atmospheric test facility.

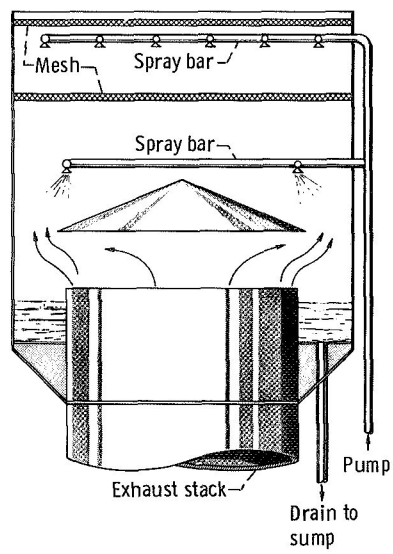


Figure 5. - Exhaust gas scrubber.

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